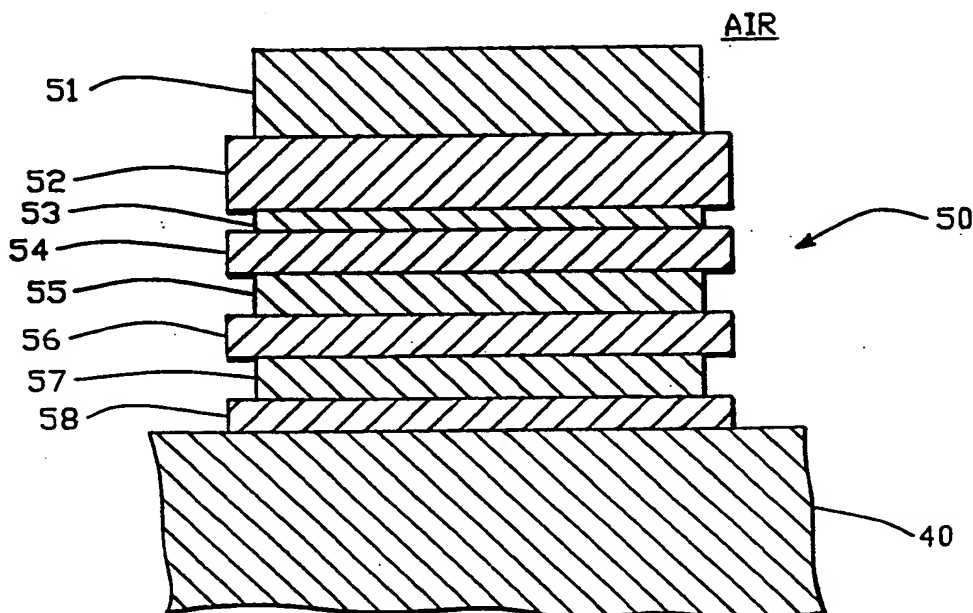




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(54) Title: ANTIREFLECTION LAYER SYSTEM WITH INTEGRAL UV BLOCKING PROPERTIES



## (57) Abstract

The present invention is directed to an antireflection and UV rejection coating. The coating comprises at least eight layers wherein adjoining layers alternate between high (58) and low (57) refractive index materials. The layer (58) adjacent an article (40) on which the coating is formed has a high refractive index greater than about 330 nanometers. The index of refractive of the low refractive index material (57) is less than about 1.50 at a wavelength of about 520 nanometers. The two layers (57, 55) of low refractive index material nearest the article each have an optical thickness at a wavelength of about 330 nm of about one-quarter wavelength.

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ANTIREFLECTION LAYER SYSTEM WITH  
INTEGRAL UV BLOCKING PROPERTIES

BACKGROUND OF THE INVENTION

5 It has been known that exposure to very bright  
sunlight can cause damage to the retina. Thus,  
sunglasses should not only reduce the level of  
visible light entering the eye but also possess  
ultraviolet (UV) light blocking capabilities.  
Surprisingly, there is no real consensus on what is  
an acceptable level of UV exposure. Some may need  
sunglasses while others do not. Those that wear  
10 sunglasses can enjoy some protection, while others,  
if the warnings are correct, may sustain some damage,  
however slight.

15 It has also been known that art and photographic  
works deteriorate when exposed for long periods to  
sunlight or even to fluorescent light. Again, there  
are no established standards concerning the time and  
level of exposure. Also, different dyes and pigments  
held in a variety of different solvents and binders  
in different works will be effected differently.

20 Various approaches have been suggested to eliminate  
or reduce the unwanted effects of UV light in these  
applications. Certain resins and plastics have been  
developed which, either due to their own structure

and composition, or when used as a host matrix for other substances which have the necessary properties, will block UV radiation by absorption. The plastic materials may be used in various ways such as a  
5 glazing material, as a laminated element in a multi-component glazing, or as an optical element in ophthalmic applications.

The typical performance of two different plastic materials, produced by the Rohm and Hass Company, Philadelphia, Pennsylvania, and designated UF 3 and  
10 UF 4, is shown in Figure 1. The longer wavelength blocking material UF 3 (curve 20) imparts a slight yellow tint. The shorter wavelength blocking material UF 4 (curve 22) imparts no perceptible tint  
15 to the transmitted light.

Resin formulations are typically based on silicon siloxane resins containing appropriate additives. They are designed to be coated on glass or UV transparent plastic by spinning or roll coating and  
20 then are heat cured. The performance of such products compares with the plastic materials UF 3 and 4.

Certain special glass compositions have also been developed which through the use of oxides of cerium  
25 and other materials will effectively block UV radiation. The use of these glass compositions seems to be confined to space and military applications, such as protective covers for silicon solar cell arrays. These compositions apparently have not been  
30 used extensively for corrective spectacles, sunglasses, or as protective glazings for art and photographic works.

The present invention relates to a special thin film multilayer structure which is dispersing and absorbing in the near ultraviolet region of the spectrum. The structure may be deposited as a coating in a single operation. It provides antireflection and UV blocking properties.

It may be applied to a wide range of glasses and plastics, and it does not require any special formulations of these materials. It offers a more economical means of providing both UV and anti-glare protection than if these properties were realized by separate process steps or separate structural elements.

The present invention makes use of the fact that the refractive index and absorption coefficient of certain dielectric materials rises rapidly at wavelengths shorter than 450 nanometers (nm). It is an improvement over the type of multilayer coating described by Rock in U.S. Patent No. 3,432,225 and Sulzbach in U.S. Patent No. 3,565,509, both of which are hereby incorporated by reference. The coatings disclosed in those patents use two or more relatively thin films to replace the quarter wave film next to the substrate in the classical three layer "Quarter, Half, Quarter" system. This system was originally described by Lockhart and King in "Three-Layered Reflection-Reducing Coatings", J. Opt. Soc. Am., Vol. 37, pp. 689-94 (1947), which is also incorporated herein by reference.

The Lockhart and King structure comprises three films in which the outer film has an optical thickness of approximately one-quarter wavelength in the visible spectrum and a refractive index (N) less

than that of a glass substrate ( $N=1.52$ ). The second film has an optical thickness of one-half wavelength and a relatively high refractive index, e.g. on the order of 2.10. The third or inner film has an optical thickness of one-quarter wavelength and a refractive index less than that of the second or half-wave film but greater than the glass substrate, e.g., on which the structure is deposited.

The Rock structure, described in U.S. Patent No. 3,432,225, replaces the inner film adjacent the substrate of the Lockhart and King structure with two films. The refractive index of the innermost film of the two films is equal to that of the half-wave film. The other film has a refractive index equal to the low index outer film. The thickness relationship of the films is altered slightly to optimize performance. Specifically, the optical thickness of the two outermost films remain about the same, while the optical thickness of the two innermost films are each about one-eighth of a wavelength at 520 nm (the design wavelength). The two-film substitution is effective not only in simulating the index of the film that has been replaced but also provides an additional reflecting boundary which extends the effective spectral range of the structure. The total optical thickness of the Lockhart and King, and Rock structures are very nearly the same.

#### SUMMARY OF THE INVENTION

The present invention is directed to an anti-reflection and UV rejection coating. The coating comprises at least eight layers wherein adjoining layers alternate between high and low refractive index materials. The layer adjacent an article on which the coating is formed has a high refractive

index greater than about 2.10 at a wavelength of about 520 nm and greater than about 2.50 at a wavelength of about 330 nm. The index of refraction of the low refractive index material is less than about 1.50 at a wavelength of about 520 nm. The two layers of low refractive index material nearest the article each have an optical thickness at a wavelength of about 330 nm of about one-quarter wavelength. The coating may be formed on one or both surfaces of an article such as a transparent substrate.

The present invention, in its simplest form, involves replacing the film next to the substrate in a Lockhart and King structure with a system of six layers, having a total thickness of approximately three-quarters of a wavelength in the green region of the spectrum, i.e., at about 520 nm. The present invention may also be viewed as replacing the base film in a Rock-type structure with a system of five layers.

Two of the films of the system of the present invention, the innermost low index films, are held at a specific optical thickness, each equal to about one-quarter wavelength at a wavelength of approximately 330 nm. The thicknesses of the remaining films are adjusted and optimized using, preferably, computer optimization techniques to provide the lowest possible reflection across the visible spectrum. The thicknesses of the remaining films in the basic Lockhart and King structure are also modified to accommodate the substitution which has replaced the base film.

Fixing the thickness of the two, innermost low index films in the base structure causes the phase relationship with the high index films to be such that the strong dispersion of the high index films is amplified, causing a very rapid rise in the reflection value in the near UV. This combined with the increase in absorption at even shorter wavelengths reduces UV transmission to less than 10% per surface at 350 nm. The effect is even more dramatic when both surfaces are coated which is usual in antireflection coating practice.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is graph illustrating transmission values for certain UV absorbing plastic materials.

Figure 2 is a graph illustrating reflectance values for certain multilayer dielectric structures.

Figure 3 is a graph illustrating reflectance values for a certain multilayer film structure.

Figure 4 schematically illustrates an embodiment of the present invention.

Figures 5 and 6 are graphs illustrating the transmittance and reflectance values, respectively, for a Rock-type structure.

Figures 7 and 8 are graphs illustrating transmittance and reflectance values, respectively, for the structure shown in Figure 4.

Figure 9 schematically illustrates another embodiment of the present invention.



Figures 10 and 11 are graphs illustrating transmittance and reflectance values, respectively, for the structure of Figure 9.

5       Figures 12 and 13 are graphs illustrating transmittance and reflectance values, respectively, for another embodiment of the present invention.

Figures 14 and 15 are graphs illustrating transmittance and reflectance values, respectively, for yet another embodiment of the present invention.

10       DESCRIPTION OF THE PREFERRED EMBODIMENTS

An understanding of the present invention is best gathered from considering certain properties of multilayer, dielectric structures known as long wavelength pass filters. Specifically, these are  
15       multilayer assemblies of alternating layers of transparent high and low refractive index (N) materials. The basic structure of such a system is:

$$(0.5H \ L \ 0.5H)^n \quad (1)$$

In Equation (1), H represents a layer of high index material having an optical thickness of one-quarter wavelength at some wavelength  $\lambda_0$ , and L represents a  
20       layer of low index material having an optical thickness of one-quarter wavelength at the same wavelength  $\lambda_0$ . Therefore, 0.5H is one-eighth of one wavelength thick at the wavelength  $\lambda_0$ . The three  
25       layers in parentheses are called the basic group. The superscript n is called the group repetition number. If n were, for example, three, the structure would be:

0.5H L H L H L 0.5H

(2)

5 The structure will provide a wavelength selective reflection value which is a function of the ratio of the high (H) and low (L) refractive index values and the group repetition number  $n$ . The reflection bandwidth of the structure is dependent on the refractive index ratio only. Figure 2 is a plot of the reflection versus wavelength for systems of hypothetical non-absorbing, non-dispersive materials with indices of refraction of 2.3 (H) and 1.46 (L). Curves 24 and 26 represent structures having group repetition numbers  $n = 2$  and 8, respectively, wherein the structures have been deposited on one side of a glass article or surface. The index of refraction of the glass is 1.52, and curves 24 and 26, like the remaining plots discussed herein, are based on computational rather than experimental data. The refractive index and extinction coefficient values used in the computations are accepted values in the art for such computations.

25 It can be seen from the curves 24 and 26 that as  $n$  increases, the ripples or modulations in the passband increase. Note that when  $n = 2$  (curve 24) only one ripple appears in the visible spectral region, and that when  $n = 8$  (curve 26) three ripples are evident.

30 Techniques have been devised for optimizing transmission and reducing passband modulation. See Baumeister P.W., 1958 J. Opt. Soc. Am. 48, 955-58. These techniques involve symmetrically and gradually varying the film thicknesses from the center film in the stack or structure to the extremities or outer films of the stack. The more films in the stack, the

smaller the differences between the films, and therefore, the more accurate must the deposition of an individual film be.

5 If the center film is reduced and the thickness of the film on either side of it is increased, while all other films retain their original thickness, only the ripple nearest the reflection band edge will be reduced, while the remaining ripples may even be increased. The variation in thickness of these  
10 films from nominal can be quite substantial, up to 15 percent, and the actual value of the change is less important than in the case where all films in the stack are varied to reduce all ripples. This design device was first presented in Austin R.R., 1975 Proc. SPIE 50, 143-52.  
15

The reflection versus wavelength plot (curve 28) for a structure using this technique is shown in Figure 3. Again, the hypothetical non-dispersive, non-absorbing refractive indices of 2.3 (H) and 1.46  
20 (L) were used in computing the plot. The group repetition number  $n$  was set at 8 and the center film was decreased in thickness by 15 percent, while the films on either side were increased in thickness by 15 percent.

25 In the concept of the present invention, a three film structure with the two outer films fixed at an optical thickness appropriate to cause a reflection increase in a desired wavelength range, and the center film varied to cause a reflection decrease in  
30 a desired transmission range, is very important. Such a structure can easily be integrated into typical broadband, multilayer, antireflection coating systems to reinforce the reflection rise on the short

wavelength side of the antireflection zone without a significant compromise in antireflection performance.

5 Previously, a structure was discussed wher the group  
repetition number  $n$  was 2, i.e. a five film system  
with three main films bounded by two films having a  
thickness substantially less than one-quarter wave.  
It was shown that only one ripple is present in the  
10 visible spectrum. This is the region in which it is  
desired to maximize transmission and reduce  
reflection. This ripple is, in fact, the nearest  
ripple to the stop band, i.e. the region of very low  
or no transmission.

15 The structure 30 of the present invention is shown in  
Figure 4. It includes eight films or layers 31-38  
formed on the surface of a glass substrate or article  
40. The five films 34-38 nearest the substrate may  
be viewed as the three film structure discussed  
above. These five films are bounded by two films 32  
20 and 33 which can be varied in thickness to  
facilitate integration into a broad band,  
antireflection structure. The result is that even  
though the thickness of the two low index films 35  
and 37 is held constant, at an appropriate thickness,  
25 and the remaining film thicknesses allowed to vary, a  
computer optimization of the film thicknesses, with  
the goal of providing the lowest possible reflection  
in the visible spectral range, will also produce a  
maximum reflection. Additionally, due to the strong  
30 absorption of UV light by the high refractive index  
films 34, 36 and 38, low transmission at wavelengths  
shorter than 390 nm will be produced.

It should be noted that the target of the optimization is to reduce the reflection in the visible spectrum to as low a value as possible. The UV reflection enhancement is provided by the constraint of the thickness of the fifth and seventh layers 35 and 37. Following the optimization procedure, the thickness relationship of the films no longer resembles the more usual forms of multilayer, antireflection coatings as seen from U.S. Patent Nos. 3,565,509 and 3,960,441.

Some resemblance to the multilayer, long wavelength, pass filter structure is evident in the fifth, sixth and seventh layers 35, 36 and 37, although these would constitute only the center fraction of such a structure. This provides a reduction of the first sideband reflection in the transmission zone at the expense of an increase in reflection in the other sidebands.

In the present invention, the system of eight films functions as an integrated whole. In one embodiment, it yields extremely low reflection over the entire visible spectrum and beyond the red extreme of the spectrum. This performance is comparable with the best results produced by conventional, multilayer, antireflection coatings. That is, the antireflection performance of the present invention is not significantly compromised by the requirement to provide UV blocking.

It should be realized that conventional multilayer, antireflection coatings do not come close to providing the UV blocking capabilities of the present invention. To illustrate this point, before any examples of the present invention are presented,

reference is made to Figur 5, which shows the wavelength versus transmission plot (curve 42) for a thin glass sheet ( $N \approx 1.52$ ) having a four layer, Rock-type coating. This coating uses titanium dioxide ( $\text{TiO}_2$ ) as the high index material and silicon dioxide ( $\text{SiO}_2$ ) as the low index material, and is deposited on each surface of the glass sheet. The reflection versus wavelength plot (curve 44) of such a structure is shown in Figure 6.

It should also be realized that if weakly dispersive films, non-absorbing in the near UV region of the spectrum, for example zirconium dioxide, were used for the high index material, many more films and a significantly greater layer thickness would be required to effect the UV blocking and the rapid transition from the blocking region to the transmission region. This can be seen from the seventeen layer ( $n = 8$ ) example of Figure 3.

#### Example 1

In this embodiment of the present invention, the goal is to provide the best antireflection performance across the visible spectrum.

The structure is shown in Figure 4. The materials used were titanium dioxide ( $N=2.35$  at 520 nm and 2.90 at 330 nm) in its anatase form as the high refractive index material and silicon dioxide ( $N=1.46$  at 520 nm) as the low index material. Titanium dioxide is the preferred material because of its refractive index and because it is so dispersive; i.e., its refractive index changes with the wavelength of incident light. The optimized thicknesses of the eight layers 31-38 in structure 30 are shown in Table 1. The thicknesses are given as fractions of a wavelength

( $\lambda_0$ ), in this case 330 nm, which shows the significant grouping of four layers 34-37 close to an optical thickness of one-quarter wavelength at 330 nm. This is the primary mechanism contributing to the onset of UV blocking.

TABLE 1

Layer #	Material	Index (N)	Optical Thickness $\lambda_0 = 330$ nm
Incident Medium (Air)			
1	SiO <sub>2</sub>	L	0.395859 $\lambda_0$
2	TiO <sub>2</sub>	H	1.088748 $\lambda_0$
3	SiO <sub>2</sub>	L	0.173525 $\lambda_0$
4	TiO <sub>2</sub>	H	0.242913 $\lambda_0$
5	SiO <sub>2</sub>	L	0.250000 $\lambda_0$
6	TiO <sub>2</sub>	H	0.225679 $\lambda_0$
7	SiO <sub>2</sub>	L	0.250000 $\lambda_0$
8	TiO <sub>2</sub>	H	0.103993 $\lambda_0$
Substrate (Glass N = 1.52)			

Figure 7 illustrates how the wavelength versus transmission curve 46 for a glass sheet having a refractive index approximately equal to 1.52 would appear if the film structure of Example 1 were coated on both sides. Figure 8 (curve 48) shows the total reflection from the two surfaces. The reflection value from both surfaces does not exceed 0.5 percent anywhere in the visible spectrum. The transmission is less than 10 percent at wavelengths shorter than 370 nm and essentially zero at wavelengths shorter than 350 nm. The transmission value is 98 percent or greater throughout the visible spectrum. This ensures that the transmission color of the coated glass is not significantly changed.

#### Example 2

This embodiment is illustrated in Figure 9. The structure 50 again includes eight layers 51-58 deposited, for example, on a glass substrate 40. In

this embodiment, some constraint has been placed on the thickness of the second film 52. The reasons are twofold. First, to reduce the structure's total thickness and thus make it more economical to produce. Second, to increase UV blocking and cut on edge steepness, i.e. the slope of the response curve 60 at the 50 percent transmission point 61 (see Figure 10), in anticipation that the optimized thickness would be closer to a quarter-wave multiple at 330 nm.

The optimized film thicknesses are shown in Table 2. As can be seen, a significant reduction of the thickness of layer 52 has been realized at the expense of only slight increases in the thickness of the other layers of structure 50. The total optical thickness in this embodiment is  $2.143\lambda_0$  compared with  $2.730\lambda_0$  for the embodiment of Example 1.

TABLE 2

Layer #	Material	Index (N)	Optical Thickness $\lambda_0 = 330 \text{ nm}$
Incident Medium (Air)			
1	SiO <sub>2</sub>	L	0.458737
2	TiO <sub>2</sub>	H	0.336784
3	SiO <sub>2</sub>	L	0.157281
4	TiO <sub>2</sub>	H	0.315573
5	SiO <sub>2</sub>	L	0.250000
6	TiO <sub>2</sub>	H	0.238724
7	SiO <sub>2</sub>	L	0.250000
8	TiO <sub>2</sub>	H	0.136298
Substrate (Glass N = 1.52)			

Figure 10 illustrates how the wavelength versus transmission curve 60 for a glass sheet having a refractive index approximately equal to 1.52 would appear if structure 50 were coated on both sides of the glass. Figure 11 (curve 62) shows the total reflection from both glass surfaces. The result of



reducing the thickness of layer 52 has been to considerably narrow the reflection band. It can be seen that while the reflection value is less than 1.5 percent at 425 nm, the violet extreme of the visible spectrum, it rises to 3 percent at 675 nm, the red extreme of the spectrum. The ultraviolet rejection performance is significantly improved from that of Example 1 in that less than 1 percent transmission occurs at 365 nm or less with 10 percent or less at 380 nm.

### Example 3

In this embodiment, structure 50 is modified by increasing all film thicknesses by the same percentage. This moves the transmission cut on edge to a slightly longer wavelength. The film thicknesses shown in Table 3 are optically the same as the thicknesses shown in Table 2. The wavelength ( $\lambda_0$ ) of the film fractional thicknesses, however, has been increased from 330 nm to 340 nm.

20

TABLE 3

Layer #	Material	Index (N)	Optical Thickness $\lambda_0 = 340 \text{ nm}$
Incident Medium (Air)			
1	SiO <sub>2</sub>	L	0.458737
2	TiO <sub>2</sub>	H	0.336784
3	SiO <sub>2</sub>	L	0.157281
4	TiO <sub>2</sub>	H	0.315573
5	SiO <sub>2</sub>	L	0.250000
6	TiO <sub>2</sub>	H	0.238724
7	SiO <sub>2</sub>	L	0.250000
8	TiO <sub>2</sub>	H	0.136298
Substrate (Glass N = 1.52)			

Figure 12 shows how the wavelength versus transmission curve 64 for a glass sheet having a refractive index approximately equal to 1.52 would appear if this structure were coated on both sides of

the glass. Figure 13 (curve 66) shows the total reflection from both surfaces of the glass. Note that the reflection curve is higher at the blue end of the spectrum than at the red end, which will impart a pronounced purple color to the reflected light even though the overall reflection value would still be much less than 1.0 percent. Furthermore, the longer wavelength location of the transmission cut-on, i.e. the wavelength location at the 50 percent transmission point, causes some transmission reduction at the blue end of the spectrum which imparts a pale yellow color to the transmitted light.

The structure of this example would probably be more useful in ophthalmic applications than in art glazings, as in the latter application maintaining a minimal reflection color is important. Nevertheless, the structure will provide UV blocking and antireflection properties comparable with that realized through laminated assemblies of antireflection-coated glass with acrylic blocking filters such as UF-3. The present invention accomplishes this combination of properties using only a coating operation.

#### 25     Example 4

A further performance improvement can be realized by using the basic structural parameters of Example 3 and substituting magnesium fluoride ( $\text{MgF}_2$ ) as the low index material ( $N=1.38$ ). This provides for a steeper cut-on edge and improvements in the bandwidth of the antireflection region. The optimized film thicknesses are shown in Table 4. The transmission versus wavelength plot (curve 68) is shown in

Figure 14, and the reflection versus wavelength plot (curve 70) is shown in Figure 15.

TABLE 4

5	Layer #	Material	Index (N)	Optical Thickness $\lambda_0 = 340 \text{ nm}$
	Incident Medium (Air)			
	1	MgF <sub>2</sub>	L	0.500471
	2	TiO <sub>2</sub>	H	0.219616
	3	MgF <sub>2</sub>	L	0.213652
10	4	TiO <sub>2</sub>	H	0.253475
	5	MgF <sub>2</sub>	L	0.250000
	6	TiO <sub>2</sub>	H	0.210004
	7	MgF <sub>2</sub>	L	0.250000
	8	TiO <sub>2</sub>	H	0.113960
15	Substrate (Glass N = 1.52)			

It can be seen that the optimization process has resulted in film layers 2 through 7 having approximately equal thicknesses and the outer low index film layer having an optical thickness of about one-half wave of ultraviolet light. This arrangement affords a high degree of steepness in the cut-on edge with a minimum number of layers and thickness.

The examples given herein evidence titanium dioxide (TiO<sub>2</sub>) as a suitable high refractive index material and silicon dioxide (SiO<sub>2</sub>) and magnesium fluoride (MgF<sub>2</sub>) as suitable low index materials. It will be apparent to those skilled in the art that variations of the design are possible using other materials. The requirement for the high index material is that it have a high dispersion and absorption in the near UV region of the spectrum, and be transparent in the visible region. Materials exhibiting these properties include, but are not limited to, cerium oxide, bismuth oxide, zinc oxide, zinc sulfide, and iron oxide. As noted, the preferred material is titanium dioxide. The low refractive index material

should, in general, have as low a refractive index as possible consistent with a reasonable level of durability. Other low index materials include, but are not be limited to, thorium fluoride, aluminum oxyfluoride and magnesium oxyfluoride.

It should be pointed out that while the examples shown comprise only two different materials in a particular design, similar structures could be designed with two or more high index materials and/or two or more low index materials, or even a material such as aluminum oxide of some intermediate refractive index.

In certain cases, it may be advantageous to use mixtures of materials or complex compounds. A mixture of cerium oxide and zinc oxide could be used for the high index films and a mixture of silicon dioxide and magnesium fluoride for the low index films. Other mixtures might be chosen to suit a particular deposition technique or to take advantage of a particular optical or physical property of a material.

While common plate glass has been used as the substrate material in the computational examples described above, variations of the invention could be deposited on plastic materials or special glasses that may be required for ophthalmic or other applications.

Modifications of the design concept are also possible. The design may be improved by adding, subtracting, subdividing, or altering the thickness of one or more layers. The designs may be modified, for example, to provide a flatter response in the

visible, antireflection band or to change the location or the slope of the reflection cut-on edge.

5 The examples provided have been chosen for compatibility with in-line sputtering as well as thermal evaporation techniques. However, it should be evident, given the range of possible useful materials, that any of the common deposition film techniques, chemical or physical, could be used alone or in combination to deposit layer systems according to the present invention. Examples might include, but are not limited to: wet chemical immersion, chemical vapor deposition, plasma assisted chemical deposition, ion plating, and ion beam deposition.

15 Examples have been shown of an invention based on a unique multilayer film structure which integrates effective blocking of ultraviolet radiation into a highly efficient antireflection coating. The total optical thickness of the structures in the examples range from a maximum of 1.7 wavelengths of green light (wavelength  $\lambda_g = 520$  nm) to  $1.27\lambda_g$ . Conventional high efficiency, broad band, antireflection coatings, without UV blocking properties, and designed only with the goal of reduced reflection, range in total optical thickness from  $0.9\lambda_g$  to  $1.5\lambda_g$ . Thus, the present invention provides UV blocking with a total thickness increase of only approximately 30 percent. Additionally, the multilayer structure of the present invention is no more complex than the most complex of conventional designs. The present invention has application in providing UV protection and antireflection properties for corrective and protective eyewear. The invention also has application in providing protection from

photochemical damage to works of art while additionally providing reduced glare from the protective glazing.

5 The present invention has been described in terms of a number of embodiments. The invention, however, is not limited to the embodiments depicted and described. Rather, the scope of the invention is defined by the appended claims.

## WHAT IS CLAIMED IS:

1. An antireflection and ultraviolet light absorbing coating, comprising:

5 at least eight layers wherein adjoining layers alternate between high and low refractive index materials;

10 the index of refraction of said high refractive index materials greater than about 2.10 at a wavelength of about 520 nanometers and greater than about 2.50 at a wavelength of about 330 nanometers;

the index of refraction of said low refractive index materials less than about 1.50 at a wavelength of about 520 nanometers; and

15 the two layers of low refractive index material nearest a surface on which the coating may be formed each having an optical thickness at a wavelength of about 330 nanometers of about one-quarter of a wavelength.

20 2. The coating of Claim 1 wherein said high refractive index material is titanium dioxide.

3. The coating of Claim 1 or 2 wherein said low refractive index material is silicon dioxide.

25 4. A coating formed on the surface of a substantially transparent substrate, comprising:

at least eight layers of alternating high and low refractive index materials such that each layer has a refractive index different from that of any adjoining layer;

30 the layer adjacent said substrate having a high refractive index and each layer of high refractive index material formed of titanium dioxide;

the index of refraction of each layer of low refractive index material less than about 1.50 at a wavelength of about 520 nanometers; and

5 the two layers of low refractive index material nearest said substrate each having an optical thickness at a wavelength of about 330 nanometers of about one-quarter of a wavelength.

10 5. The coating of Claim 4 wherein said low refractive index material is selected from the group consisting of: silicon dioxide, magnesium fluoride, thorium fluoride, aluminum oxyfluoride, and magnesium oxyfluoride.

15 6. An antireflection and ultraviolet light absorbing coating formed on a surface of an article, comprising:

eight layers of alternating high and low refractive index materials such that each layer has a refractive index different from that of any adjoining layer;

20 the eighth layer of material adjacent said article having a high refractive index greater than 2.10 at a wavelength of about 520 nanometers and greater than about 2.50 at a wavelength of about 330 nanometers.

25 the seventh layer of material having a low refractive index less than about 1.50 at a wavelength of about 520 nanometers and an optical thickness at a wavelength of about 330 nanometers of about one-quarter of a wavelength,

30 the sixth layer of material having said high refractive index; and

the fifth layer of material having said low refractive index, and an optical thickness at a



wavelength of about 330 nanometers of about one-quarter of a wavelength.

7. The coating of Claim 6 wherein said high refractive index material is titanium dioxide.

5 8. The coating of Claim 7 wherein said low refractive index material is silicon dioxide.

1 / 8

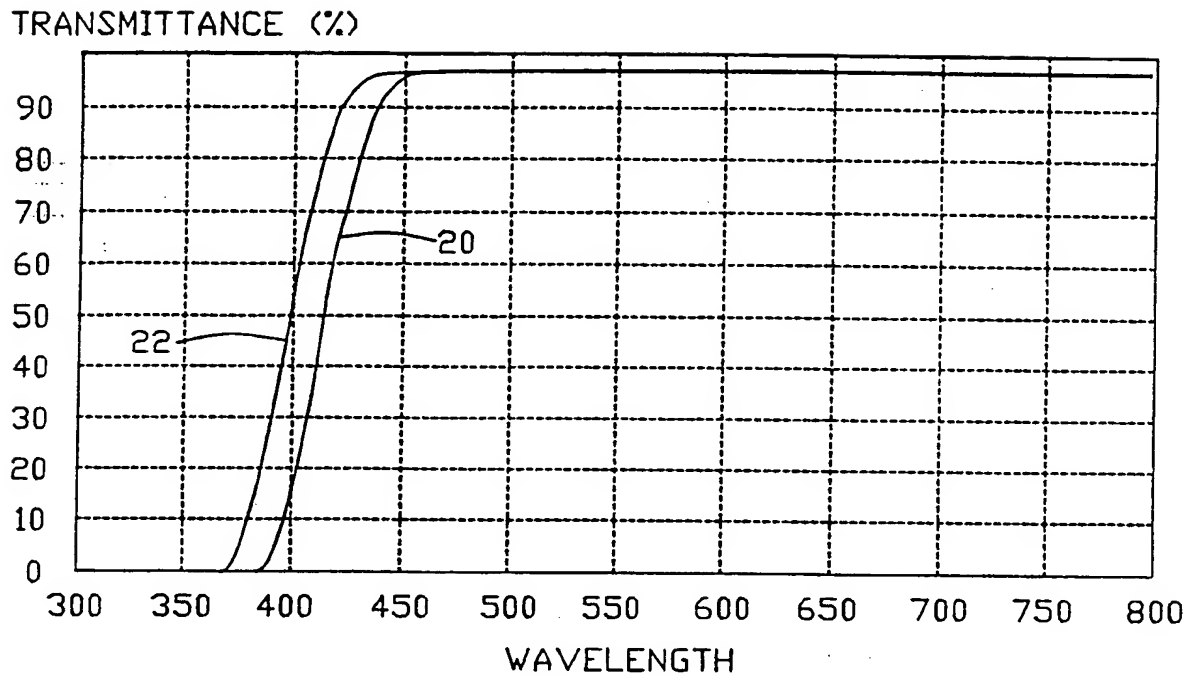


FIG.-1

SUBSTITUTE SHEET

2 / 8

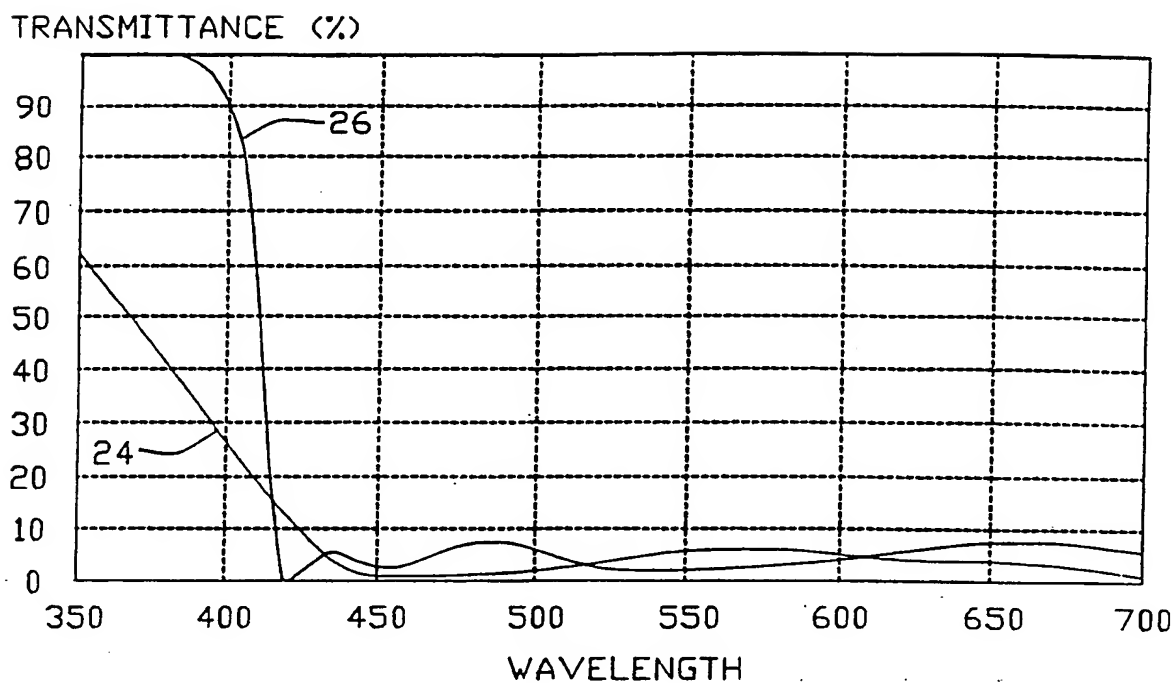


FIG.-2

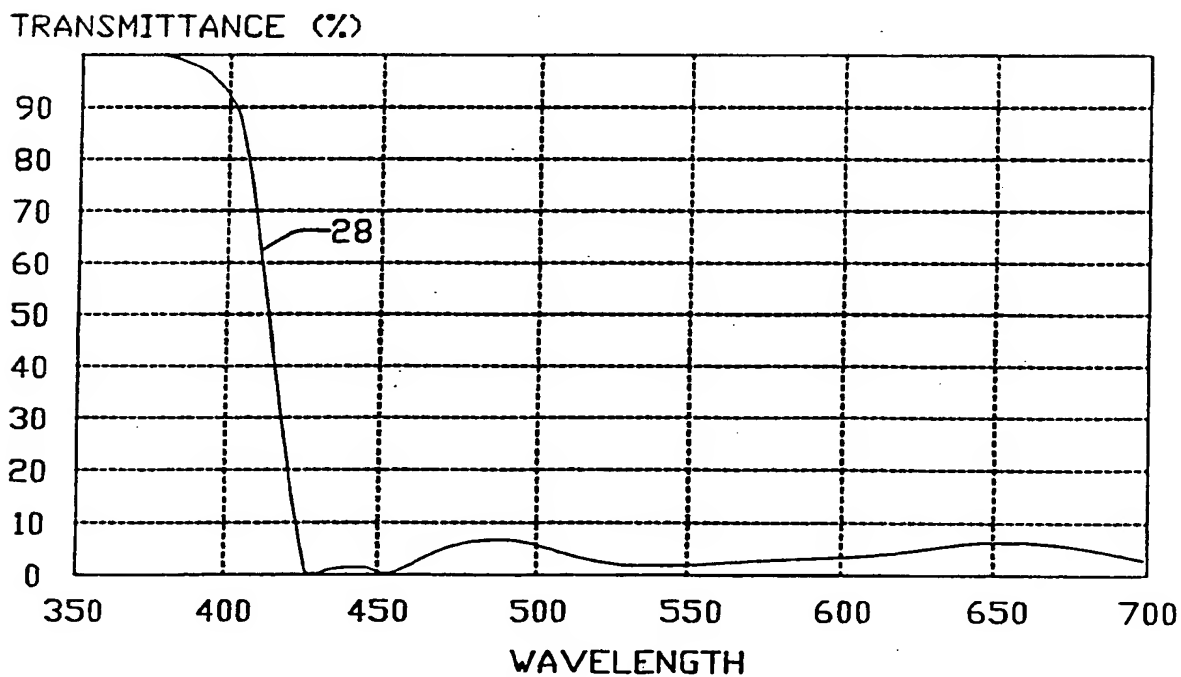


FIG.-3

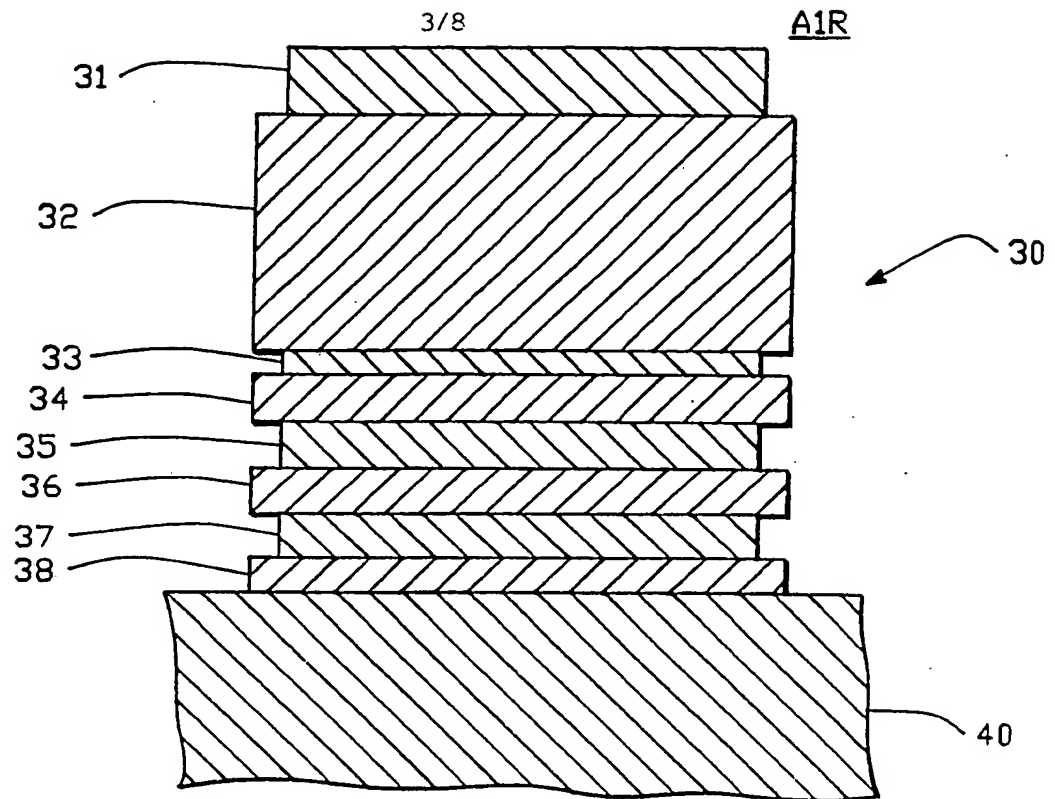


FIG.-4

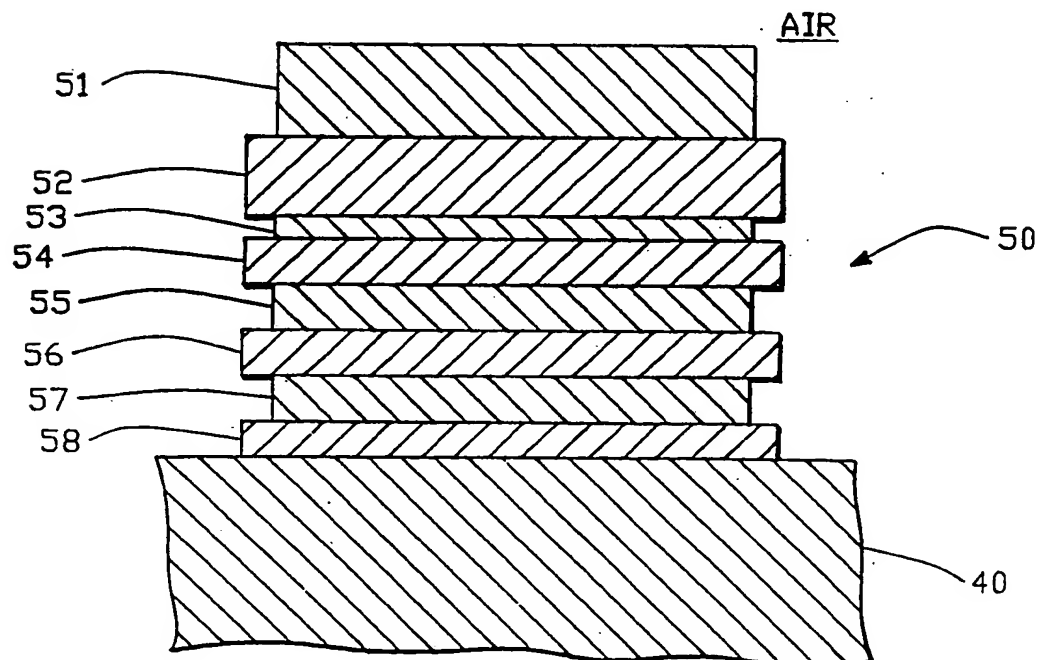


FIG.-9

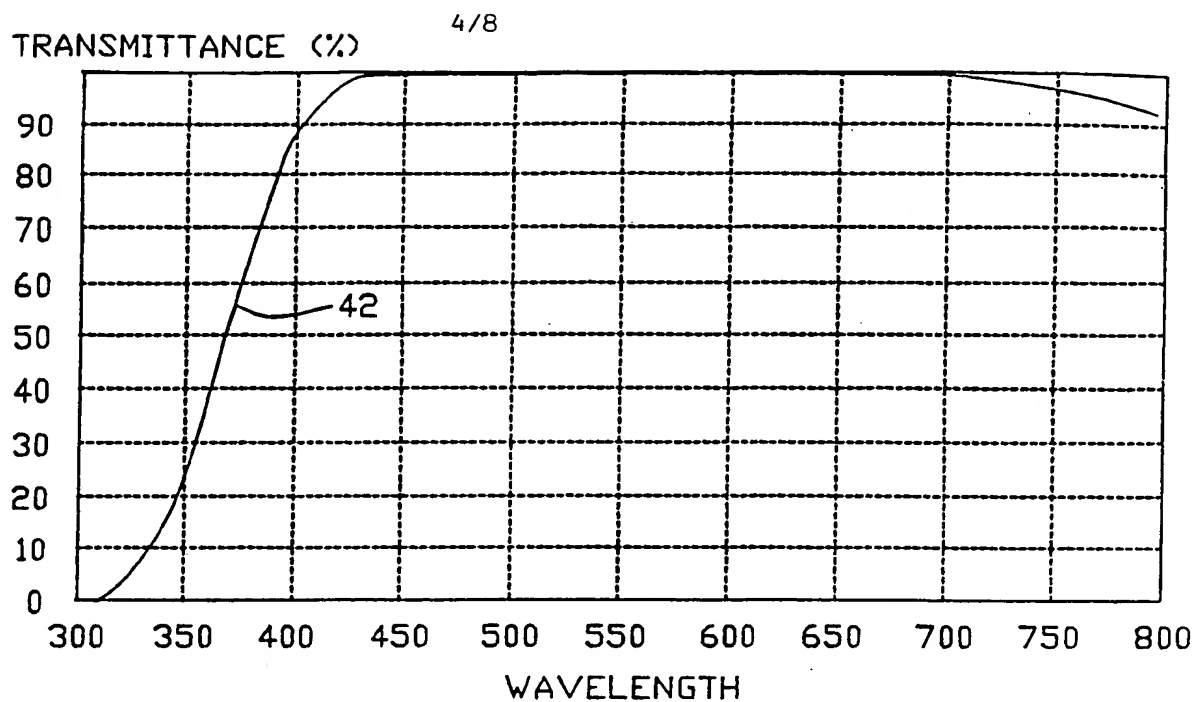


FIG.-5

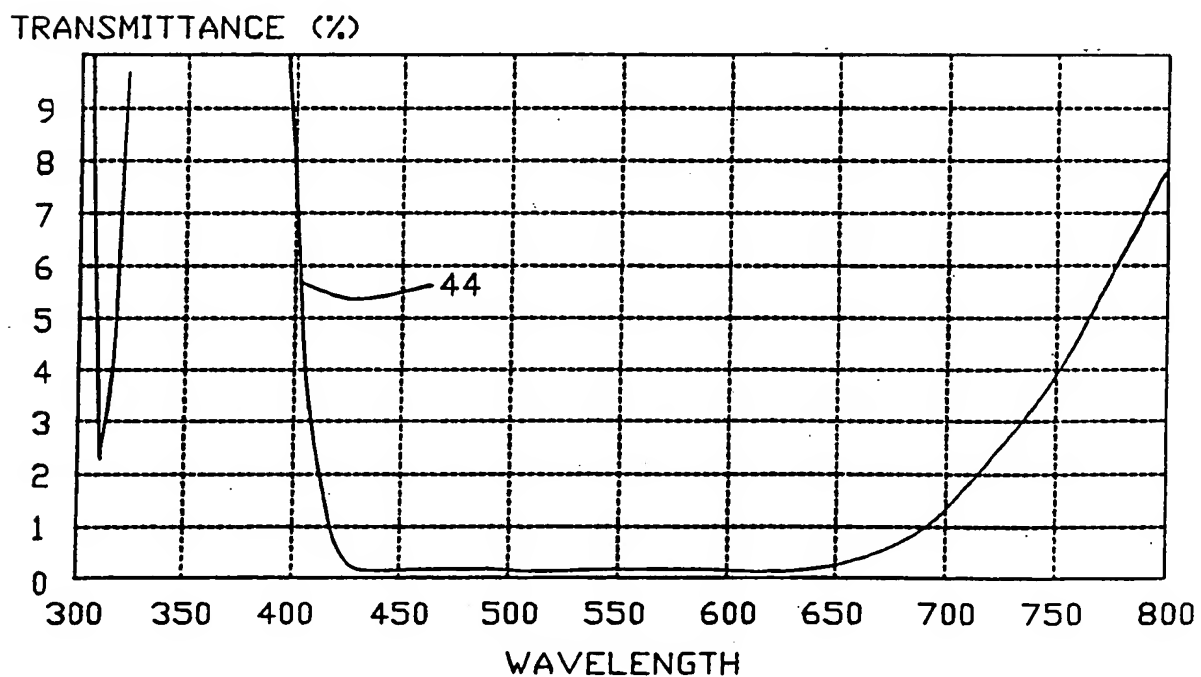


FIG.-6

5/8

TRANSMITTANCE (%)

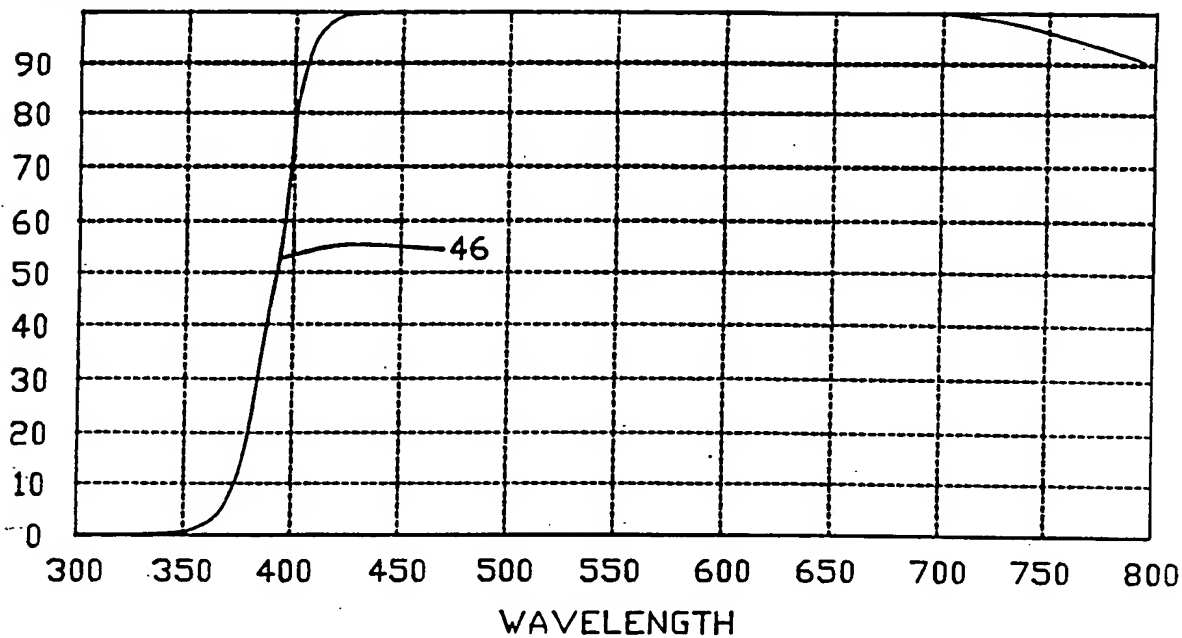


FIG.-7

TRANSMITTANCE (%)

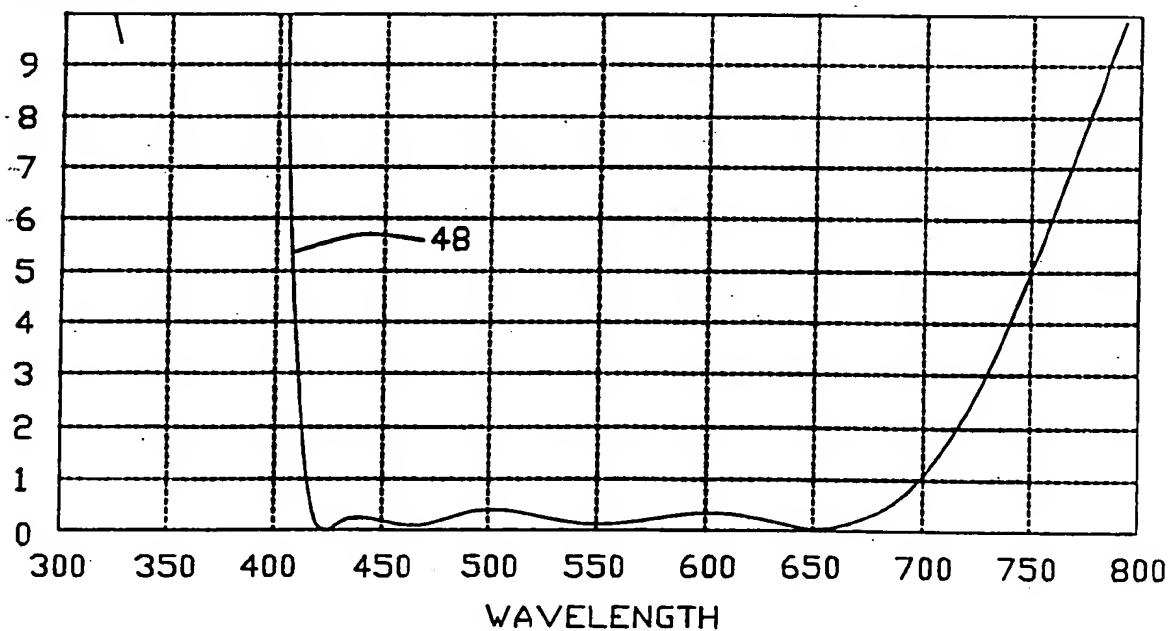
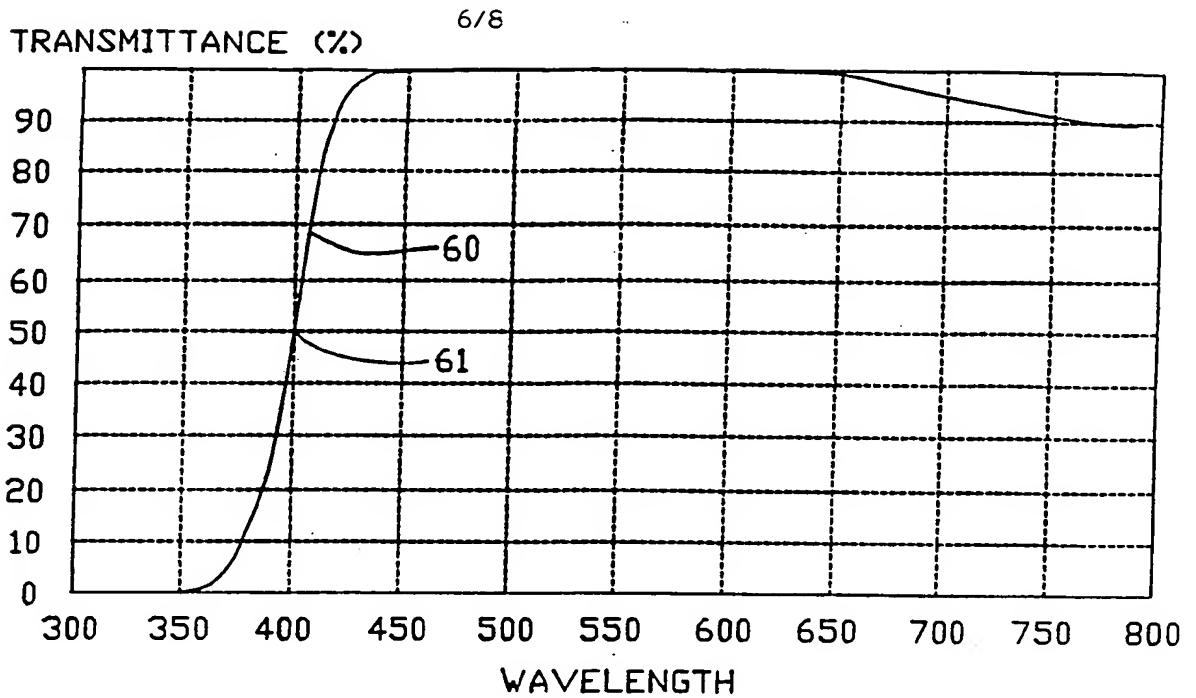
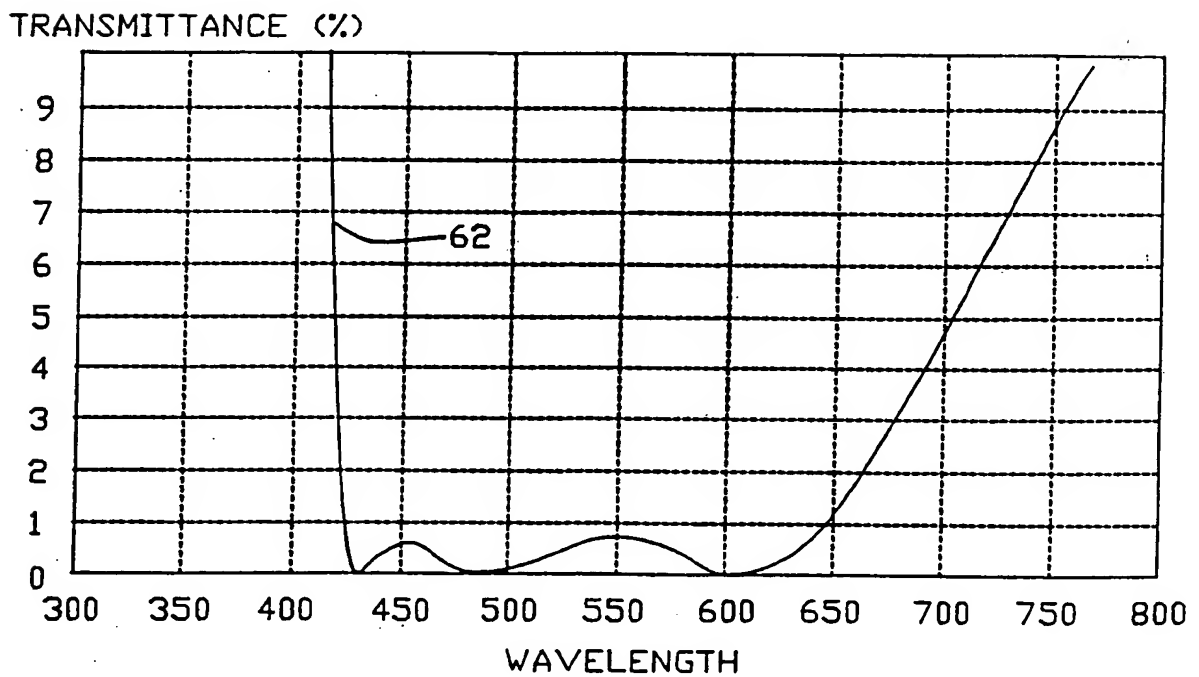


FIG.-8

SUBSTITUTE SHEET

**FIG.-10****FIG.-11****SUBSTITUTE SHEET**

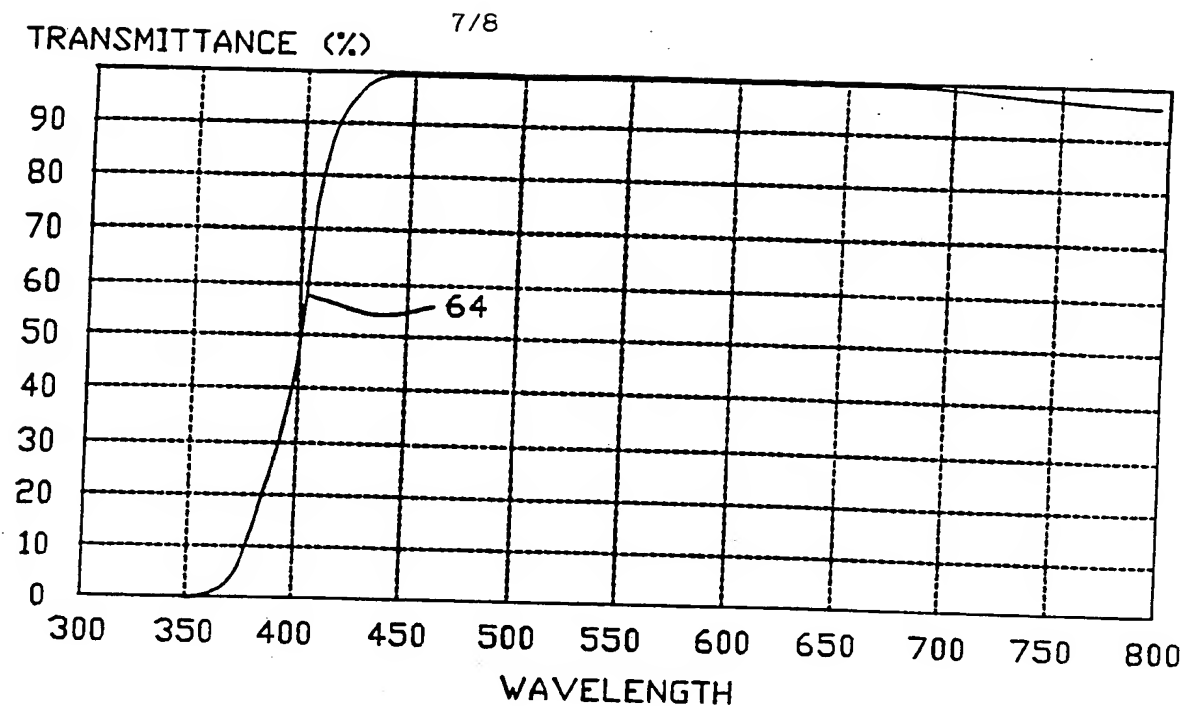


FIG.-12

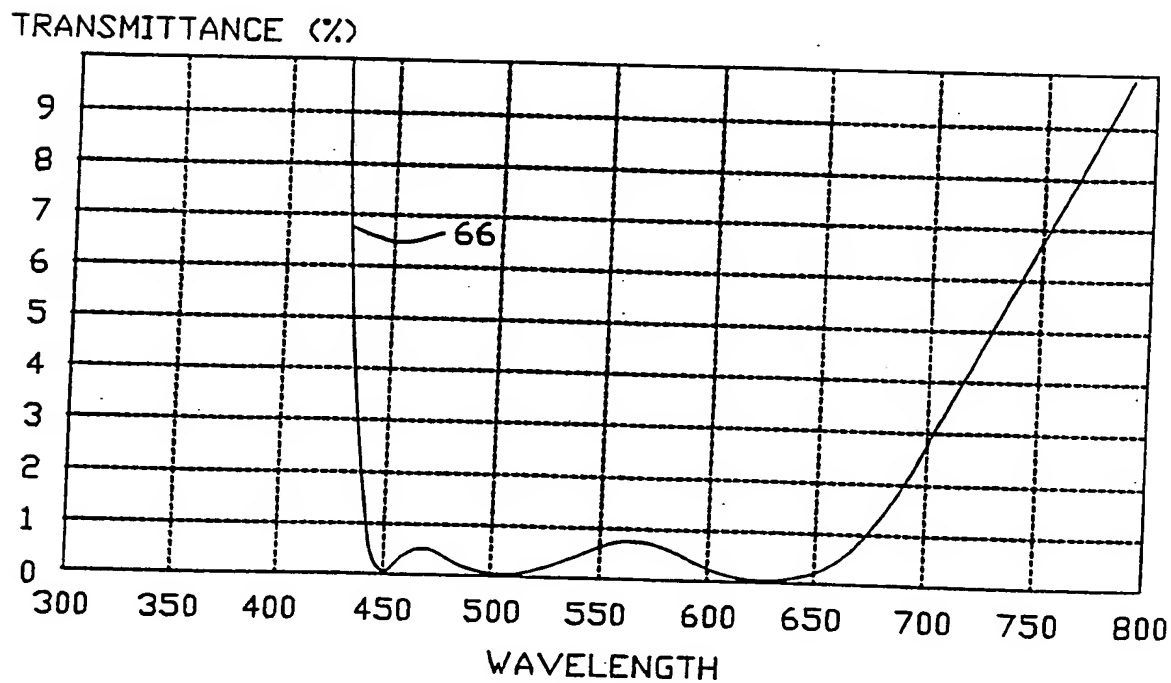


FIG.-13

SUBSTITUTE SHEET



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TRANSMITTANCE (%)

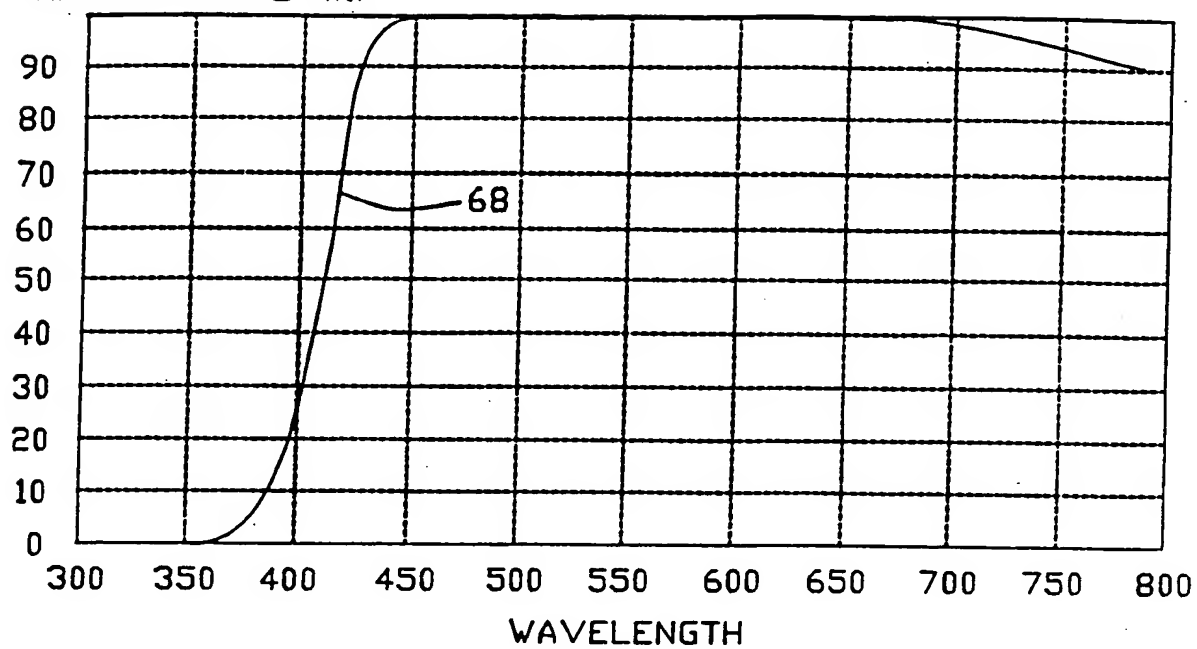


FIG.-14

TRANSMITTANCE (%)

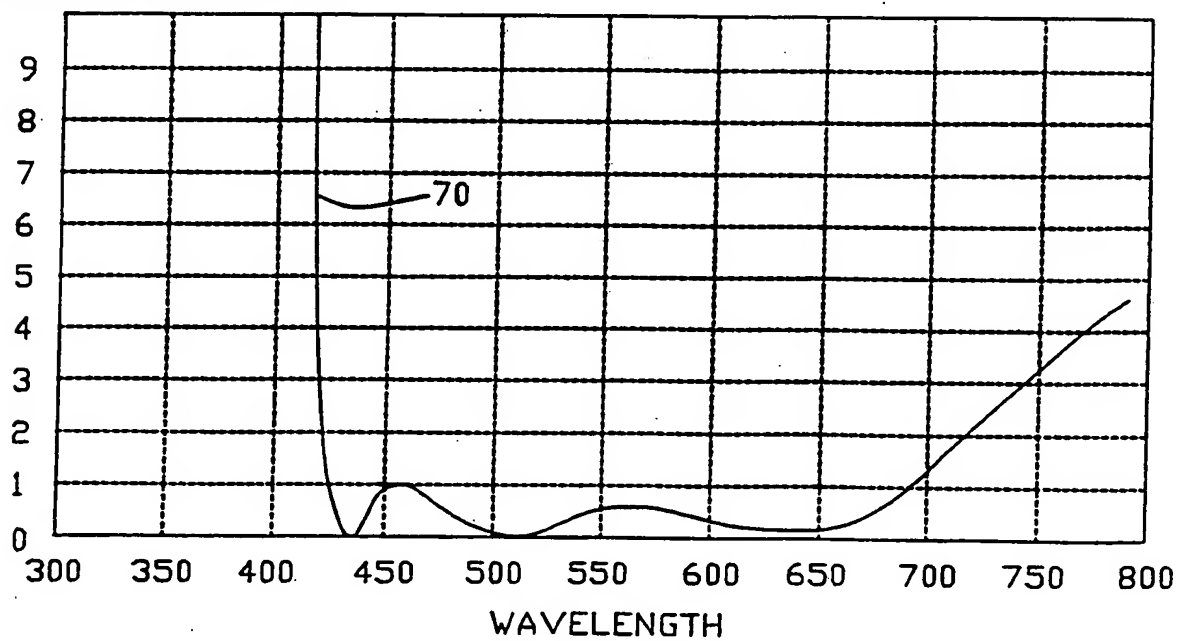


FIG.-15

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US90/06780

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC <div style="margin-left: 40px;">           IPC (5): B32B 9/00            U.S. CL. 428/212         </div>																	
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; margin-top: 10px;">Minimum Documentation Searched <sup>7</sup></div> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%;">Classification System</th> <th style="width: 80%;">Classification Symbols</th> </tr> <tr> <td style="text-align: center; vertical-align: middle;">U.S.</td> <td>           350/1.6, 165, 166            428/212, 411.1, 446, 448, 432, 913         </td> </tr> </table> <div style="text-align: center; margin-top: 10px;">Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched <sup>8</sup></div>			Classification System	Classification Symbols	U.S.	350/1.6, 165, 166 428/212, 411.1, 446, 448, 432, 913											
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<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%;">Category <sup>10</sup></th> <th style="width: 70%;">Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup></th> <th style="width: 20%;">Relevant to Claim No. <sup>13</sup></th> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 4,793,669 (PERILLOUX) 27 DECEMBER 1988; See entire document.</td> <td style="text-align: center; vertical-align: top;">1-8</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y,P</td> <td>US, A, 4,896,928 (PERILLOUX ET AL) 30 JANUARY 1990; See entire document.</td> <td style="text-align: center; vertical-align: top;">1-8</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 4,609,267 (DEGUCHI ET AL) 02 SEPTEMBER 1986; See entire document.</td> <td style="text-align: center; vertical-align: top;">1-8</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 4,168,113 (CHANG ET AL) 18 SEPTEMBER 1979; See entire document.</td> <td style="text-align: center; vertical-align: top;">1-8</td> </tr> </table>			Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	Y	US, A, 4,793,669 (PERILLOUX) 27 DECEMBER 1988; See entire document.	1-8	Y,P	US, A, 4,896,928 (PERILLOUX ET AL) 30 JANUARY 1990; See entire document.	1-8	Y	US, A, 4,609,267 (DEGUCHI ET AL) 02 SEPTEMBER 1986; See entire document.	1-8	Y	US, A, 4,168,113 (CHANG ET AL) 18 SEPTEMBER 1979; See entire document.	1-8
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Y	US, A, 4,168,113 (CHANG ET AL) 18 SEPTEMBER 1979; See entire document.	1-8															
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>																	
<b>IV. CERTIFICATION</b> <table style="width: 100%;"> <tr> <td style="width: 50%; vertical-align: top;">           Date of the Actual Completion of the International Search   <div style="text-align: center; font-weight: bold;">18 DECEMBER 1990</div> </td> <td style="width: 50%; vertical-align: top;">           Date of Mailing of this International Search Report   <div style="text-align: center; font-weight: bold; font-size: 1.2em;">11 FEB 1991</div> </td> </tr> <tr> <td style="vertical-align: top;">           International Searching Authority   <div style="text-align: center; font-weight: bold;">ISA/US</div> </td> <td style="vertical-align: top;">           Signature  Authorized Officer   <div style="text-align: center; font-weight: bold;">P.J. Ryan</div> </td> </tr> </table>			Date of the Actual Completion of the International Search  <div style="text-align: center; font-weight: bold;">18 DECEMBER 1990</div>	Date of Mailing of this International Search Report  <div style="text-align: center; font-weight: bold; font-size: 1.2em;">11 FEB 1991</div>	International Searching Authority  <div style="text-align: center; font-weight: bold;">ISA/US</div>	Signature  Authorized Officer  <div style="text-align: center; font-weight: bold;">P.J. Ryan</div>											
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